



## Review

## Catalytic reactions of gamma-valerolactone: A platform to fuels and value-added chemicals



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## ABSTRACT

Gamma-valerolactone (GVL), which is accessible from renewable lignocellulosic biomass, has been identified as one of the most promising platforms for the sustainable production of fuels and value-added chemicals. This review aims at recent advances in the catalytic production of GVL from biomass and further upgrading of GVL to fuels as well as value-added chemicals. The first part briefly reviews recent advances for the production of GVL from biomass. The second and third sections critically review and identify current technologies for the efficient production of GVL. The mechanism, different types of advanced homogeneous and heterogeneous catalysts employed have been compared and broadly categorized. Challenges and areas that need improvement are also highlighted in the corresponding area. The fourth section concentrates on potential applications and the upgrading of GVL to fuel additives, diesel fuels and value-added chemicals. The final section offers a summary and future perspective in the field.

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## Nomenclature

LA	levulinic acid
BL	butyl levulinate
GVL	$\gamma$ -valerolactone
EL	ethyl levulinate
HMF	5-hydroxymethylfurfural
ML	methyl levulinate
BF	butyl formate
FAME	fatty acid methyl esters
DMF	2,5-dimethylfuran
ILs	ionic liquids
MTBE	methyl tert-butyl ether
WHSV	weight hourly space velocity
MTHF	2-methyltetrahydrofuran
Zr-Betal-100	Betal zeolite with the Si/Zr ratio of 100
THF	tetrahydrofuran
DOE	department of energy
$Y_{\text{GVL}}$	yield of $\gamma$ -valerolactone
NREL	National Renewable Energy Laboratory
1,4-PDO	1,4-pentanediol
ZrO <sub>2</sub> -VS	acid-tolerant ZrO <sub>2</sub>

## 1. Introduction

It has been predicted that 20% of transportation fuel and 25% of chemicals by 2030 will be produced from lignocellulosic biomass, which is the only renewable carbon source capable of replacing fossil fuels [1–3]. Lignocellulosic biomass, consisting of three main structural units (i.e., cellulose, hemicellulose and lignin), is a complex fibrous material that can be found in the cell walls of plants as shown in Fig. 1 [4–6]. As an alternative carbon source, lignocellulosic biomass offers some more attractive benefits over petroleum [7,8]. Lignocellulosic biomass is cheap, abundant and has widespread worldwide availability. It is reported that 1.3 billion tons of dry biomass can be produced per year in the United States alone [8]. More importantly, the lignocellulosic biomass is sustainable and its derived monomers can be transformed into fuels and numerous valuable chemicals [9–14]. The main pathway of the conversion of biomass feedstocks into renewable fuels was shown in Fig. 2 [13,15]. Over the last several decades, catalytic conversion of biomass has got significant growth and will likely increase in the coming years [16–21].

Due to the structural and chemical complexity of lignocellulosic biomass, various advanced processes have been employed to convert it into fuels and chemicals [12,13,20]. Current tech-

nologies mainly involve two major routes: thermal processing and aqueous phase processing (Fig. 2). Thermal processing including gasification and pyrolysis, is well-suited for the production of fuels, where inaqueous phase processing provides attractive paths for the production of intermediates that can be subsequently upgraded to value-added chemicals and fuels for the transportation sector [13,20]. Biomass gasification often provides clean combustion, compact burning equipment, and high thermal efficiency [22–25]. However, the gasification process is quite complex and sensitive, where the fuel is bulky and frequent refueling is often required for continuous running of the system. Besides, the way of dealing with the residues such as ash and tarry condensates is a time consuming and tough job [20,22,24]. Unlike gasification, pyrolysis process consists of a thermal degradation of the initial solid biomass into gases and liquids without an oxidizing agent [21,26]. The products of biomass pyrolysis primarily consist of biochar, bio-oil and gases including CH<sub>4</sub>, H<sub>2</sub>, CO and CO<sub>2</sub> [27,28]. Pyrolysis offers a flexible and attractive way of converting solid biomass into an easily stored and transported liquid fuels [29]. However, the cost of pyrolysis is quite high compared to the production of fossil fuel. Despite the rapid development over the last few decades has been reached, many techno-economic barriers (e.g., the cost of biomass pyrolysis) need be reduced [30,31].

In comparison, aqueous phase processing of biomass seems more promising and attractive. The DOE/NREL report, named “Top Value Added Chemicals from Biomass” [32] has identified a list of top value-added chemical candidates for launching renewable chemical platforms derived from biomass. Along the line of these candidates, GVL has attracted considerable attention over the last several decades and will likely flush in the coming years due to its attractive physical-chemical properties and unique fuel characteristics as depicted in Table 1 in comparison with ethanol fuel. Over the last a few decades, a number of researchers have developed different advanced methods for improving the synthesis of GVL from lignocellulosic biomass [10,16,21,32]. GVL is stable in water and in the presence of air, and thus can also be produced from C6 and C5 sugars through LA intermediate. Besides, GVL, a widely used food additive, exhibits the most typical characteristics of an ideal sustainable green solvent for the production of either energy or carbon-based consumer products [33]. In addition, GVL does not hydrolyze under neutral conditions and does not form a measurable amount of peroxides in a glass flask under air in weeks, making it a safe material for the industrial application [33,34]. A comparative study of GVL and ethanol as fuel additives with a mixture of 10 v/v% GVL or ethanol and 90 v/v% 95-octane gasoline [33,34], has shown very similar fuel properties and it has been suggested as an attractive liquid fuel.

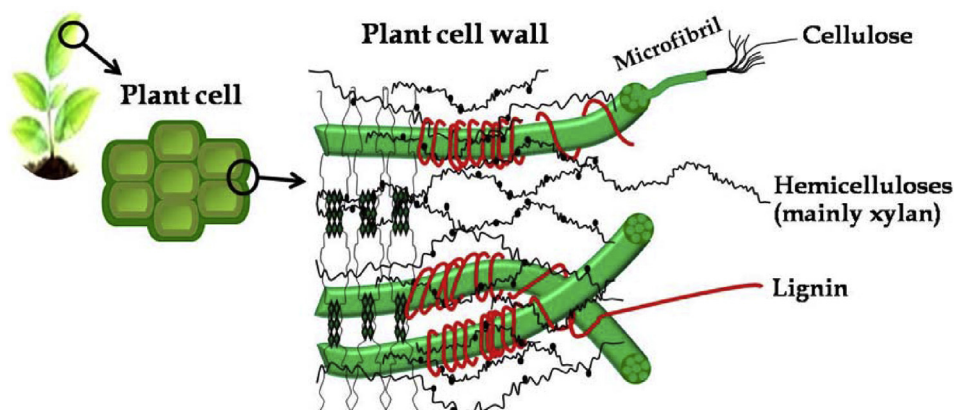


Fig. 1. Lignocellulosic biomass composition in plants. Reprinted with permission from Ref. [6].

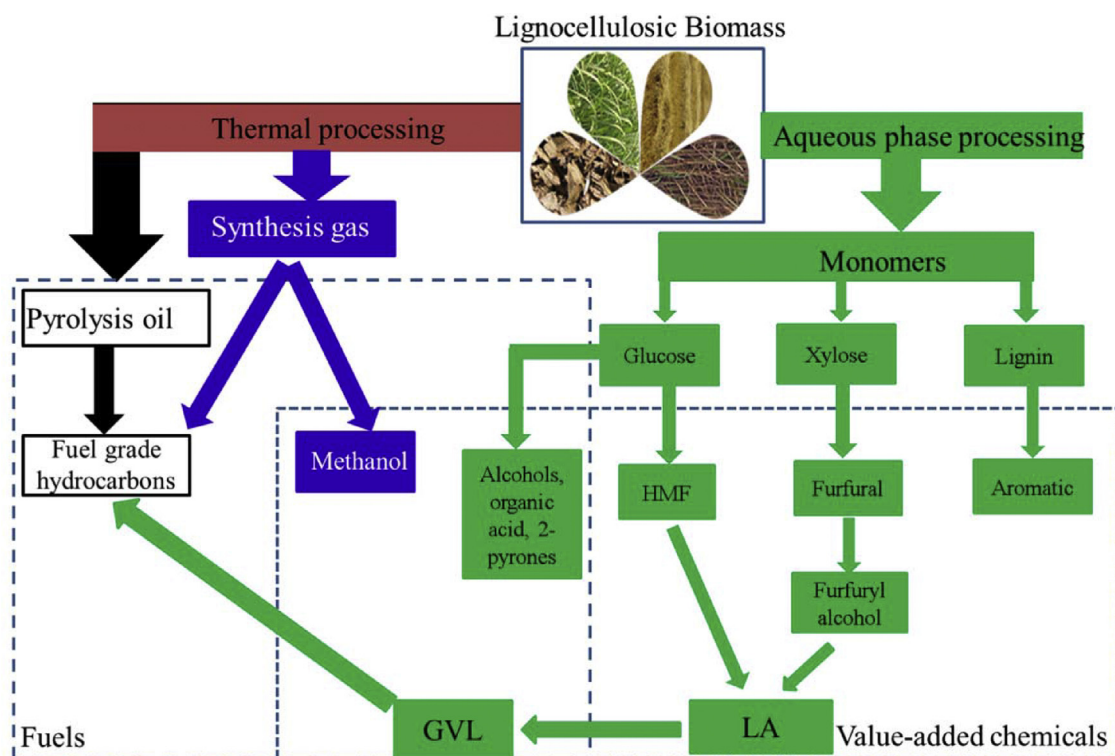


Fig. 2. Diagram of the conversion of lignocellulosic biomass through thermochemical and aqueous phase processing to fuels and value-added chemicals.

This review leans on invaluable earlier reviews on GVL manufacture, starting with several reviews [35,36–38]. For the sake of length and cohesion, we focus on our research on the current technologies to produce GVL as well as the catalytic upgrading of GVL to fuels and value-added chemicals as summarized in Scheme 1. GVL is renewable, stable and can be used as: (1) precursor of gasoline and diesel fuels, such as C8 alkanes, C9–C18 alkanes, C9 alkanes and valeric esters [1,16,35–38]; (2) green solvents in fine chemicals synthesis and food additives; (3) as an intermediate in the synthesis of a number of value-added chemicals (e.g., 1,4-pentanediol, and methyl pentenoate) [38–46].

## 2. Production of GVL using homogeneous catalysts

### 2.1. Mechanistic studies

Over the last several decades, different homogeneous catalysts have been employed for the hydrogenation of LA [47,48]. Because of the easy access to the catalytic active center, a number of groups have developed various homogeneous catalysts for this transformation. Ru-based homogeneous catalysts appeared more attractive and have been widely studied [47–50], such as  $\text{RuCl}_2(\text{PPh}_3)_3$ ,  $\text{Ru}(\text{acac})_3/\text{PBu}_3$ , and  $\text{Ru}(\text{acac})_3/\text{P}(\text{n-Oct})_3$  catalyst. One of the typical works is to use the Shvo-catalyst (Fig. 3) [48], the reaction typically involves the hydrogenation of LA to 4-hydroxypentanoic acid intermediate followed by ring-closure and the formation of GVL (Fig. 3), wherein the formic acid was often used as hydrogen donor giving 4-hydroxypentanoic acid and  $\text{CO}_2$  [49,50]. The production of hydroxypentanoic acid intermediate plays a key role in the formation of GVL. The Shvo-catalyst of  $\{[2,5\text{-Ph}_2\text{-3,4-(p-MeOPh)}_2(\eta^5\text{-C}_4\text{CO})_2\text{H}]\text{Ru}_2(\text{CO})_4(\mu\text{-H})\}$  was used for the conversion of LA into GVL. The Ru-dimer complex is actually the precursor of monomeric catalyst (Fig. 3) which contains acidic hydrogen at the cyclopentadienyl group and a hydride hydrogen on the Ru site [51–53]. It is supposed that the proton from hydrox-

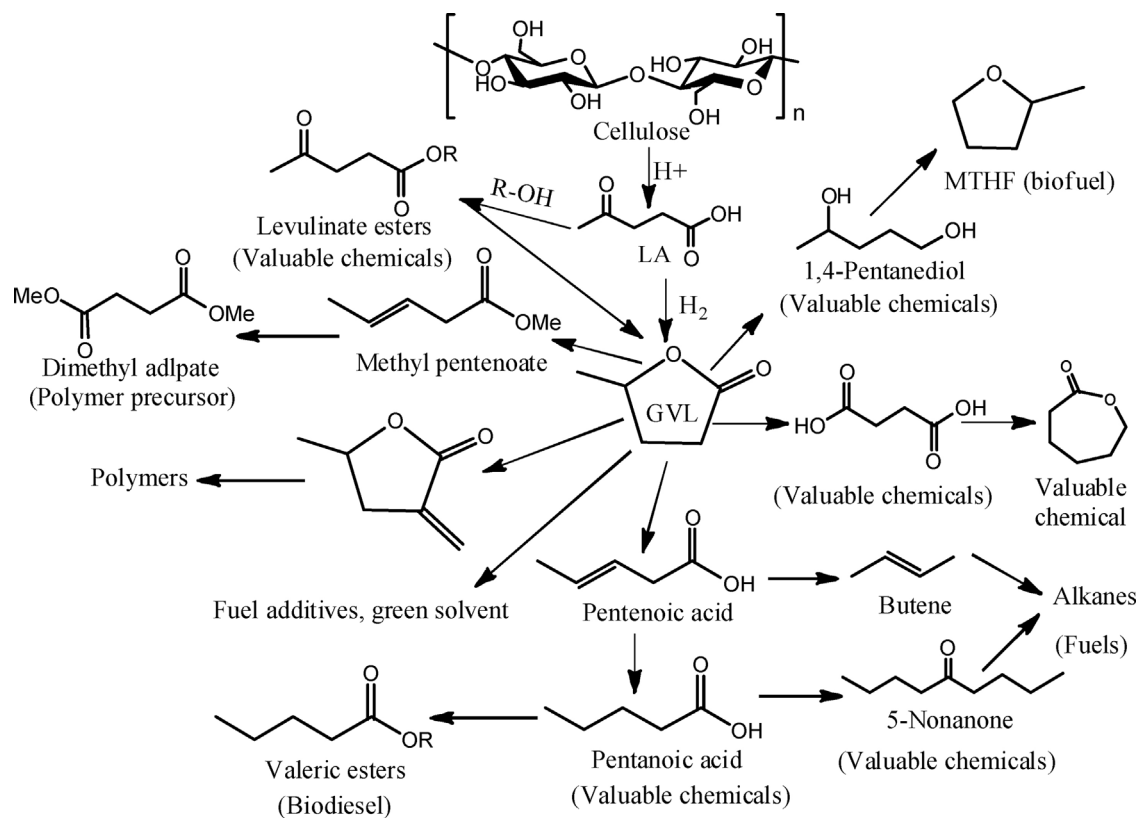
Table 1

The main physical properties of GVL in comparison with ethanol fuel.

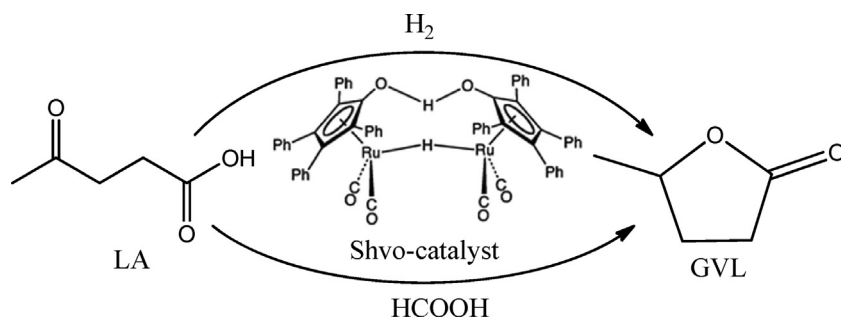
Terms	Ethanol	GVL
M ( $\text{g mol}^{-1}$ )	46.07	100.12
Carbon (wt%)	52.2	60
Hydrogen (wt%)	13.1	8
Oxygen (wt%)	34.7	32
Boiling point ( $^{\circ}\text{C}$ )	78	207
Melting point ( $^{\circ}\text{C}$ )	–114	–31
Flash Point ( $^{\circ}\text{C}$ )	13	96.1
Density ( $\text{g mL}^{-1}$ )	0.789	1.0485
Solubility in water/ (mg/ml)	miscible	$\geq 100$
Octane number <sup>a</sup>	108.6	–
Cetane number	5	–
$\Delta H_{\text{vap}}$ ( $\text{kJ mol}^{-1}$ )	42.590	–54.8
$\Delta C H^{\circ}_{\text{liquid}}$ ( $\text{kJ mol}^{-1}$ )	$-1367.6 \pm 0.3$	–2649.6

ide and the hydridic hydrogen would provide the two hydrogens for the reduction, and formic acid plays an important role in the regeneration of catalyst with losing a molecule  $\text{CO}_2$  [51].

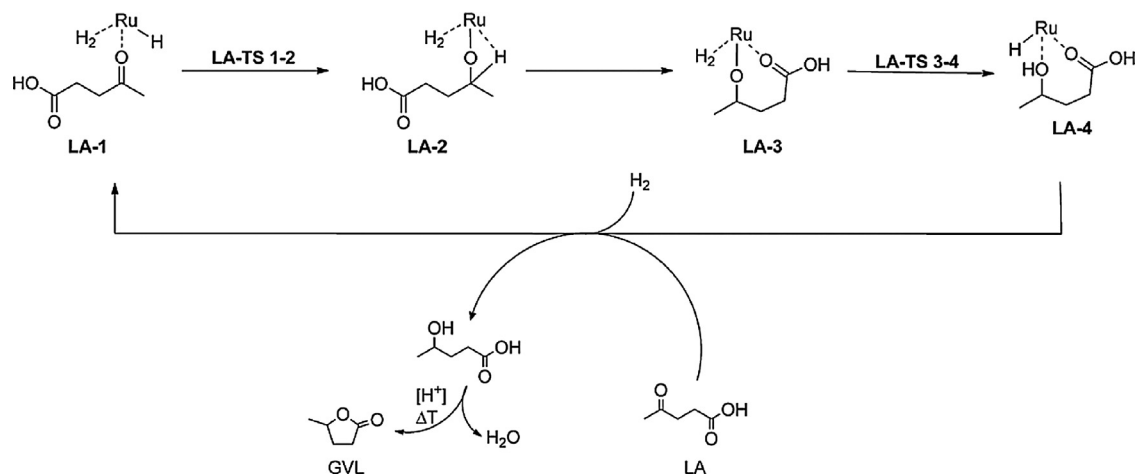
Another typical work is to use a multifunctional homogeneous catalysis system (composed of Ru based organic metal precursor  $\text{Ru}(\text{acac})_3$ , ligands and acidic additives) for highly selective and flexible catalytic conversion of LA to yield quantitative GVL in a flexible system by Geilen et al. [52]. A density functional theory (DFT) study corroborated with experimental data from catalytic processes and NMR investigations were further employed to better understand the mechanism.  $[\text{Ru}(\text{TriPhos})\text{H}]^+$  was proposed as the catalytically active unit as shown in Fig. 4 and it was considered to play a crucial role in the reduction of the  $\text{C}=\text{O}$  functionality in aldehydes, ketones, lactones, and even free carboxylic acids. They proposed hydride transfer from the Ru–H group to the carbonyl or carboxyl carbon followed by the protonation of resulting Ru–O unit via  $\sigma$ -bond metathesis from a coordinated dihydrogen molecule [52].



**Scheme 1.** Production and upgrading of GVL to fuel, fuel additives and valuable chemicals.



**Fig. 3.** The Shvo-catalyst used for hydrogenation of LA.



**Fig. 4.** Calculated catalytic cycle for the hydrogenation of LA to GVL, Using the cationic complex LA-1 as the catalyst (phosphine ligand omitted for clarity). Reproduced with permission from Ref. [52].

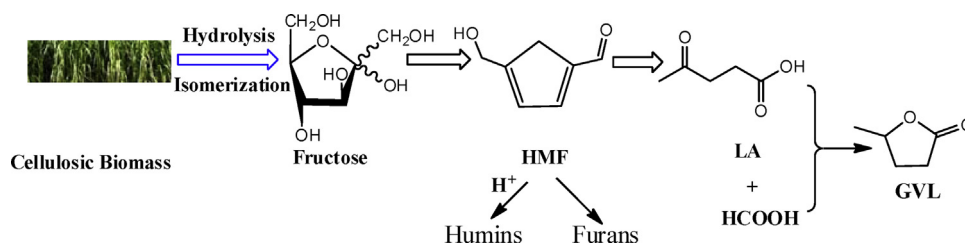
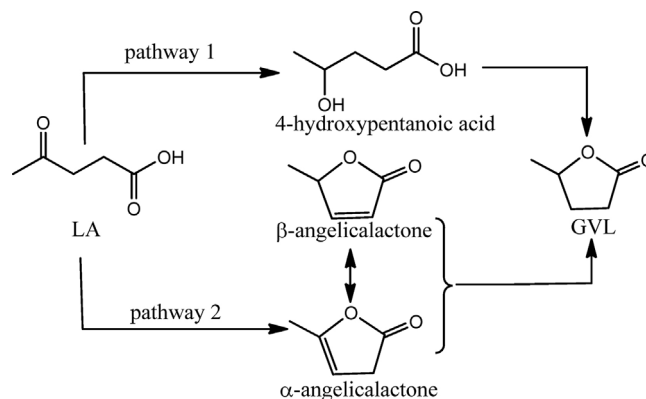


Fig. 5. Cellulosic biomass to GVL through LA and formic acid.

## 2.2. Development and advances

The biggest advantage of a homogeneous catalyst lies in the fact that it can act as a single active site, making homogeneous catalysts intrinsically more active and selective [50,52,54,55]. Ru- or Ir-based homogeneous complex such as  $\text{RuCl}_2(\text{PPh}_3)_3$ ,  $\text{Ru}(\text{acac})_3/\text{PBU}_3$ ,  $\text{Ru}(\text{acac})_3/\text{P}(\text{n-Oct})_3$  and  $[\text{Ir}(\text{COE})_2\text{Cl}]_2$  catalysts have been frequently reported with good conversion of LA and high selectivity of GVL [52,55,56]. Some pioneering works have been done by Joo et al. using water soluble ruthenium catalysts for the hydrogenation of LA using a Ru-complex catalyst based on mono-sulfonated triphenylphosphine [57]. Recently, Fu et al. reported the use of Ir-based half-sandwich complexes catalyst for the conversion of LA to GVL with good yields [58,59]. A range of different water-soluble ligands in the Ru-catalyzed hydrogenation of LA have been screened by Kühn et al., and the best catalytic performance was reported with TPPTS ligand [60]. However, it was noticed that higher turnover frequencies were obtained using ligand-free  $\text{Ru}(\text{acac})_3$ , which was presumably reduced to  $\text{Ru}(0)$  nanoparticles in the process. Heeres et al. combined the dehydration of glucose to LA using dilute TFA as the dehydration catalyst and the simultaneous hydrogenation using  $\text{RuCl}_3/\text{TPPTS}$  as catalyst under the conditions of 94 bars of  $\text{H}_2$ , wherein 19% of LA and 23% of GVL were obtained in one-step [61].

The conversion of carbohydrates directly into GVL without the isolation of intermediate LA could provide a means of producing GVL with minimal processing steps. The use of transfer hydrogenation for the in-situ hydrogenation of LA to GVL is very attractive, since formic acid is produced along with LA from the conversion of cellulosic biomass as shown in Fig. 5. However, it should also be noted that acid-catalyzed dehydration of carbohydrates could lead to the formation of insoluble humins (Fig. 5), which would influence the production of GVL in a significant manner. Rational control of the reaction rates of each step required the combination of acidic catalyst and hydrogen-transfer catalyst. Qi et al. did some pioneering works and reported that the addition of the Shvo catalyst to fructose dehydration, 55% yield of GVL was produced in one-step [49]. More typical works of the hydrogenation of LA to GVL



Scheme 2. Hydrogenation of levulinic acid based on heterogeneous catalyst.

have been depicted in Table 2. In general, the hydrogenation of LA to GVL using homogeneous catalysts often presented good activity and high selectivity under mild conditions. However, some homogeneous catalysts require multi-steps to be synthesized, which may increase the extra cost and efforts. Further researches will be needed to improve the efficient recycle of the catalyst, and enhance the catalyst durability.

## 3. Production of GVL using heterogeneous catalysts

### 3.1. Mechanistic studies of GVL production

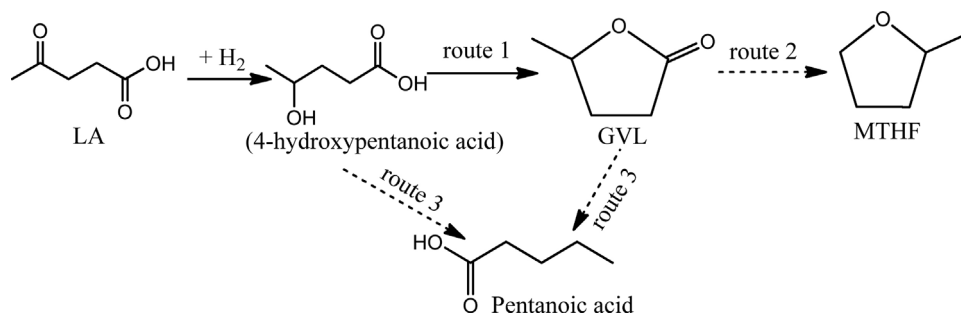
Due to its relatively easy recycle and ecofriendly property, numerous heterogeneous catalysts have also been explored and designed for the conversion of LA. Therefore, the understanding of the mechanism for the formation of GVL from LA over heterogeneous catalysts has also received increasing attentions [39,65–67]. Ru-nanoparticles have been often used to catalyze the hydrogenation reactions. There are two possible pathways for the hydrogenation of LA proposed in Scheme 2 [39,40]. It is often proposed that the first step during the hydrogenation reaction was a

Table 2  
Hydrogenation of LA using homogeneous catalysts.

No.	Substrate	Catalyst	Solvent	T (°C)	H <sub>2</sub> sources	t (h)	Y <sub>GVL</sub> (%)	Refs.
1	LA	$\text{Ru}(\text{acac})_3 + \text{TPPTS}$	$\text{H}_2\text{O}$	140	69 bars $\text{H}_2$	12	95	[47]
2	LA	$[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\text{bpy})(\text{H}_2\text{O})][\text{SO}_4]$	$\text{H}_2\text{O}$	70	$\text{HCOONa}$	18	25	[47]
3	LA	$\text{Ru}(\text{acac})_3 + \text{PBU}_3$	—	200	82.8 bars $\text{H}_2$	6	37	[47]
4	LA	$\text{Ru}(\text{acac})_3 + \text{PnOct}_3 + \text{NH}_4\text{PF}_6$	—	160	100 bars $\text{H}_2$	18	>99	[54]
5	LA	$\text{RuCl}_2(\text{PPh}_3)_3$	—	180	12 kg/cm <sup>2</sup> $\text{H}_2$	24	99	[62]
6	LA	$\text{RuH}_2(\text{PPh}_3)_4$	—	180	12 kg/cm <sup>2</sup> $\text{H}_2$	24	58	[62]
7	LA	$\text{Ru}(\text{acac})_3/\text{RP}(\text{C}_6\text{H}_4\text{-m-SO}_3\text{Na})_2^b$	—	140	10 bars $\text{H}_2$	4.5	39–100	[63,64]
8	LA	$\text{RuCl}_3 \cdot \text{H}_2\text{O}/\text{PPh}_3$	—	150	$\text{HCOOH}$	12	93	[59]
9	Glucose	$\text{Ru}(\text{CO})_4\text{I}_2 + \text{HI}$	$\text{H}_2\text{O}$	200	30 bars $\text{H}_2$	8	39.1	[55]
10	Fructose	$\text{HCO}_2\text{-CF}_3$ , Ru/C	$\text{H}_2\text{O} + \text{HCO}_2\text{-CF}_3$	180	94 bars $\text{H}_2$	8	62	[61]
11	Glucose	$\text{HCO}_2\text{-CF}_3$ , Ru/C	$\text{H}_2\text{O} + \text{HCO}_2\text{-CF}_3$	180	94 bars $\text{H}_2$	8	38	[61]
12	Sucrose	$\text{HCO}_2\text{-CF}_3$ , Ru/TPPTS	$\text{H}_2\text{O} + \text{HCO}_2\text{-CF}_3$	180	94 bars $\text{H}_2$	8	52	[61]

Note: T: temperature, t: time, Y: the yield of GVL.

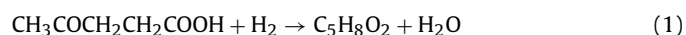




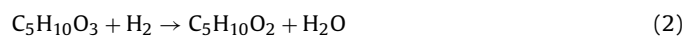
**Scheme 3.** Hydrogenation of LA to produce GVL as well as side products.

conception of molecular hydrogen and liquid LA on the metal support [39,65–70]. Hydrogen following the division of the H diatom, was adsorbed on the surface of Ru to form the bond between Ru and hydrogen, and then LA were adsorbed on the surface of Ru by the combination of Ru with carbonyl C and O atoms. When the first hydrogen atom was added to the LA, it would generate an intermediate to link to the surface of Ru by an  $\sigma$ -bond formed between carbon and Ru. Further adding another H atom would result in the formation of  $\gamma$ -hydroxyvaleric acid [61,65]. Finally, the produced  $\gamma$ -hydroxyvaleric acid would form GVL by the dehydrogenation. The second possible pathway was to form GVL's reciprocal transformation, pseudo-LA [69]. Angelicalactones ( $\alpha$ -type or  $\beta$ -type in pathway 2) would form from the endothermic dehydration of LA [71,72]. In the presence of Ru nanoparticles and continuous  $H_2$  supply, angelicalactones were anticipated to rapidly hydrogenate, forming GVL.

The advantage of heterogeneous catalysis often involves easy separation, efficient recycling, minimization of metal leaching, the improved handling and process control [67,73]. Over the last several decades, different types of heterogeneous catalysts have been designed and studied for the hydrogenation of LA and LA-derivatives to GVL [37–40,46]. Along with the hydrogenation of LA to GVL in the presence of heterogeneous catalysts, several side reactions occurred simultaneously and produced several byproducts as shown in Scheme 3. The ideal production of GVL proceeded via the reaction route 1 (Scheme 3) expressed in the equation 1:



However, to exert the hydrogenation of LA efficiently into GVL, its undesired side reaction to MTHF via the route 2 through the Eq. (2): (Scheme 3)



and the side reaction to pentanoic acid (route 3, Eq. (3)) must be avoided:



Studies have shown a critical dependency of the hydrogenation of LA via route 1 and avoiding of the side reaction of GVL via routes 2 or 3 on the catalyst used and the catalytic reaction system [70,74,75]. Abdelrahman et al. [39] studied the reaction pathways and kinetics governing the Ru-catalyzed hydrogenation of LA in the aqueous phase to produce GVL in a packed bed reactor. At temperatures below 423 K, GVL proceeded primarily through a 4-hydroxypentanoic acid (HPA)-mediated pathway where hydrogenation occurred firstly and then followed by acid-catalyzed dehydration. Apparent barriers for LA hydrogenation and HPA esterification are 48 and 70 kJ mol<sup>-1</sup>, respectively. Besides, they found that the intramolecular esterification of HPA was possible to control the rate of GVL formation at low temperatures, while mass transfer limited the rate of hydrogenation at high temperature. In this review, we mainly outline the various chemical routes

to produce GVL. The enzymic, biological and electrolytic productions of GVL are not included here.

### 3.2. Recent advances in the production of GVL using heterogeneous catalysts

#### 3.2.1. Supported noble-metal catalysts

Due to the large surface area and synergic effect between metal nanoparticle and support, the supported metal nanoparticles often present good performances in the hydrogenation. The supported Noble metal catalysts (e.g., Ru, Rh, Pd, Pt and Au) are most commonly used catalysts for the production of GVL from various substrates. Upare et al. [75] reported that carbon supported Ru, Pt and Pd Noble metal for the selective hydrogenation of LA under vapour phase in a continuous down flow fixed-bed reactor system, where 5% Ru/C catalyst gave GVL with perfect selectivity. Manzer investigated various metals supported on carbon for GVL synthesis and Ru/C catalyst display the highest activity with 97% yield at 150 °C and 34.5 bar  $H_2$  in dioxane [67]. Ir, Rh, and Pd showed the moderate activity. However, low conversions of LA were obtained by Pt, Re and Ni system (less than 15%). LA hydrogenation has also been studied in supercritical  $CO_2$  over the Ru/ $Al_2O_3$  and Ru/ $SiO_2$  catalysts giving 99% conversion with complete selectivity to GVL under conditions of 200 °C and 200 bar  $H_2$  [73]. The utilization of supercritical  $CO_2$  offers the benefits of avoiding the use of aqueous means, allowing the minimization of liquid waste generation, improving rapid separation of products [76]. By taking the advantages of  $CO_2$ , we have also fabricated a series of Pd nanoparticles supported on  $SiO_2$  and  $Al_2O_3$  support by the assistance of liquid  $CO_2$ . These catalysts have displayed good catalytic performance as well as high durability in the hydrogenation of LA [65,69,77]. Wettstein et al. [78] reported the production of LA and GVL from cellulose deconstruction using GVL as a solvent in biphasic reaction systems consisting of GVL and aqueous solutions containing HCl (0.1–1.25 M) and a solute (e.g., salt or sugar). The GVL solvent extracted the majority of the LA greater than 75%, which can subsequently be converted to GVL over a carbon-supported Ru–Sn catalyst. This approach offered no need for the separation of final products and eliminated the deposition of solid humin species in the cellulose deconstruction reactor. Du et al. [79,80] have studied different metals (e.g., Pd, Pt, Ru, Au) supported on  $TiO_2$ ,  $SiO_2$ , C, and  $ZrO_2$ . Among the various catalysts, Au/ $ZrO_2$  catalysts display the best performance in terms of high conversion with high yields of ~97%. Son et al. [72] reported the supported Au nanoparticle catalyst was efficient for the synthesis of GVL through screening a series of Ru/C, Ru/SBA, Au/ZrC and Au/ $ZrO_2$  catalysts, where over 90% yield of GVL can be obtained in water solvent. The Au/ $ZrO_2$  catalyst showed good activity and recyclability, which can be used over five runs [72]. An overview of the typical Noble metal catalysts used for the production of GVL from various substrates was depicted in Table 3. Overall, vapor phase hydrogenation is likely to be energy sensitive with the vaporization of LA (boiling point of 245–246 °C)

**Table 3**  
Production of GVL using noble-metal catalysts.

No.	Substrate	Catalyst	Solvent	T (°C)	H <sub>2</sub> sources	t (h)	Y <sub>GVL</sub> (%)	Refs
1	LA	Ru/C	Dioxane	150	34.5 bars H <sub>2</sub>	4	97	[67]
2	LA <sup>a</sup>	Ru/SiO <sub>2</sub>	H <sub>2</sub> O + CO <sub>2</sub>	200	100 bars H <sub>2</sub>	N.D.	>99	[73]
3	LA	Ru-P/SiO <sub>2</sub>	H <sub>2</sub> O	150	HCOOH	6	30	[81]
4	LA	Ru/C	H <sub>2</sub> O	150	40 bars H <sub>2</sub>	1	30	[81]
5	LA	Ru/TiO <sub>2</sub>	H <sub>2</sub> O	150	HCOOH + 40 bars H <sub>2</sub>	1	63	[81]
6	LA	Ru/C	CH <sub>3</sub> OH	130	12 bars H <sub>2</sub>	3	91	[66]
7	LA	Pd/Al <sub>2</sub> O <sub>3</sub>	---	220	HCOOH	12	29	[82]
8	LA	5% Ru/C	Dioxane	265	1–25 bars H <sub>2</sub>	50	98.6	[75]
9	LA	5% Ru/C	Dioxane	201	H <sub>2</sub> + CO <sub>2</sub> (201 bars)	N.D.	73.2	[83]
10	LA	5% Ru/Al <sub>2</sub> O <sub>3</sub>	Dioxane	201	H <sub>2</sub> + CO <sub>2</sub> (200 bars)	N.D.	75.3	[83]
11	LA	5% Rh/C	Dioxane	141	H <sub>2</sub> + CO <sub>2</sub> (247 bars)	N.D.	98.9	[83]
12	LA	5% Ir/C	Dioxane	141	H <sub>2</sub> + CO <sub>2</sub> (250 bars)	N.D.	43.0	[83]
13	LA	Au/TiO <sub>2</sub>	H <sub>2</sub> O	150	Formic acid	6	55	[79]
14	LA <sup>b</sup>	Au/ZrO <sub>2</sub> -VS	H <sub>2</sub> O	180	Formic acid	3	99	[79]
15	BL <sup>c</sup>	Au/ZrO <sub>2</sub>	H <sub>2</sub> O	170	BF	6	95	[80]
16	LA <sup>d</sup>	5% Ru/C	H <sub>2</sub> O	150	Formic acid	5	90	[72]
17	LA	5% Au/ZrO <sub>2</sub>	H <sub>2</sub> O	150	Formic acid	5	97	[72]
18	Fructose	Au/ZrO <sub>2</sub>	H <sub>2</sub> O	150	Formic acid	5	48	[72]
19	Fructose	Au/ZrC	H <sub>2</sub> O	150	Formic acid	5	47	[72]
20	Fructose	Ru/SBA-15	H <sub>2</sub> O	150	Formic acid	5	26	[72]
21	Fructose	Ru/C	H <sub>2</sub> O	150	Formic acid	5	21	[72]
22	LA	5% Au/ZrO <sub>2</sub>	H <sub>2</sub> O	140	Formic acid	5	66	[72]
23	LA	Ru–Ni/ Meso-C	---	150	45 bars H <sub>2</sub>	2	96	[84]
24	LA	5% Ru/Hydroxyapatite	H <sub>2</sub> O	70	5 bars H <sub>2</sub>	4	99	[85]

Note: Y: yield of GVL.

<sup>a</sup> N.D.: not defined.

<sup>b</sup> ZrO<sub>2</sub>-VS: acid-tolerant ZrO<sub>2</sub>.

<sup>c</sup> BL: butyl levulinate.

<sup>d</sup> BF: butyl formate.

requiring a high energy input [37]. By contrast, the liquid-phase hydrogenation is simpler and more economical [37,38]. In addition, the high dispersion of metal nanoparticle on the support has played a crucial role in their performances, thus high dispersion of the supported metal nanoparticles still requires more efforts [37].

### 3.2.2. Supported non-noble metal catalysts

As previously discussed, the precious metal catalysts often presented good catalytic performances in the production of GVL. However, the cost factor of these catalysts, usage of volatile organic additives, high pressure operations and involvement of other harsh reaction parameters limit their application in the practice. The productions of GVL by non-noble metal catalysts have gained many efforts over the last a few decades. Some of the cheap and stable non-noble metal catalysts such as RANEY® Ni and Urushibara Ni catalysts have been used for the hydrogenation of LA to yield GVL [66]. Upare et al. [86] reported the LA hydrogenation on Al<sub>2</sub>O<sub>3</sub>-supported Ni–Cu bimetallic catalysts, where high yield of GVL up to 96% was obtained. They studied the hydrogenation of LA at 265 °C and 25 bars H<sub>2</sub> over silica supported copper catalysts and observed a decline in activity during the time on stream. To overcome the deactivation during the time on stream, the catalyst has been promoted with Ni. In a patented work over a Ni catalyst, a 71% yield of GVL has been achieved by Haan et al. [87]. More recently, Mohan et al. [88] reported the LA hydrocyclisation over Ni catalysts in the vapour phase at atmospheric pressure and they investigated the effect of supports (such as Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, ZnO, ZrO<sub>2</sub>, TiO<sub>2</sub> and MgO) on the catalytic performance of LA hydrocyclisation without using any organic additives. Pyridine adsorbed IR patterns revealed the presence of both Lewis as well as Brønsted acid sites which were responsible for the dehydration of the intermediate 4-hydroxy pentanoic acid to yield GVL.

Bimetallic nanoparticle catalysts tend to display better performances for liquid phase hydrogenation of LA to GVL [89,90]. Shimizu et al. [89] tested a series of base-metal (Ni, Co, Cu, and Fe) and metal oxides (Mo, V, and W oxides) co-loaded carbon (C) and Ni-loaded metal oxides for the hydrogenation of LA to GVL.

Ni–MoOx/C pre-reduced at 500 °C showed the highest activity (99% yield and TON of 4950) and showed more than 300 times higher turnover number (TON) than previously reported Noble metal-free catalysts. Recently, Obregón et al. [90] also synthesized the Al<sub>2</sub>O<sub>3</sub> supported homo-Ni and Ni–Cu bimetallic catalysts for the hydrogenolysis of LA, where the highest yield of GVL with 96% was obtained under the conditions of 250 °C, 6.5 MPa and 2 h. These studies further suggest that bimetallic nanoparticle catalysts are much better for the production of GVL.

Except the widely used Ni-derived bimetallic catalysts, Cu-derived bimetallic catalysts have also attracted many attentions. Recently, we have shown that the Cu-derived bimetallic catalysts were highly efficient for the hydrogenation of LA as well as furfural [9,68,91,92], where the Cu-catalysts were facilely synthesized from Cu-hydroxalate (like CuCr-, CuAl-, CuFe-) precursors. The hydroxalate consist of the hydroxides of two or more different kinds of metal cations with lamellar structure. The cation-exchange ability of the Brucite layer enabled the production of high amount of Cu in the supported catalysts through the calcination and reduction. Recently, Hengne et al. [93] reported nanocomposites of Cu–ZrO<sub>2</sub> and Cu–Al<sub>2</sub>O<sub>3</sub> quantitatively catalyzed the hydrogenation of LA and its methyl ester to give 90–100% selectivity to GVL in methanol and water respectively. More typical works are compared in Table 4. At present, the biggest issue of this type of catalysts is the leach of active metal and the high yield of coke produced during the process. Increasing the synergic effects between metal nanoparticle and support would be necessary to improve the activity in the future studies.

### 3.2.3. Other types of catalysts

Other types of heterogeneous catalysts for the selective production of GVL have also received great progress in the production of GVL. Chromium containing copper catalysts have been widely utilized due to their high thermal stability and long lifespan [95,96]. Chia et al. [97] studied a series of metal oxides (e.g., ZrO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, MgO/ZrO<sub>2</sub>, MgO/Al<sub>2</sub>O<sub>3</sub>, CeZrOx) that were efficient for the hydrogenation of levulinate esters into GVL. Among these metal oxides

**Table 4**

Production of GVL using the supported non-noble metal catalysts.

No.	Substrate	Catalyst	Solvent	T (°C)	H <sub>2</sub> sources	t (h)	Y <sub>GVL</sub> (%)	Refs.
1	LA	Raney Ni	--	~200	48.3 bars H <sub>2</sub>	N.D.	94	[94]
2	LA	Raney Ni	---	220	48 bars H <sub>2</sub>	3	94	[95]
3	LA	Ni-MoOx/C	--	140	8 bars H <sub>2</sub>	5	97	[89]
4	LA	Ni/TiO <sub>2</sub>	--	140	8 bars H <sub>2</sub>	5	38	[89]
5	LA	Ni-MoOx/C	toluene	140	8 bars H <sub>2</sub>	5	21	[89]
6	LA	Cu/SiO <sub>2</sub>	--	265	10 bars H <sub>2</sub>	--	99.9	[86]
7	LA	Cu-ZrO <sub>2</sub>	H <sub>2</sub> O	200	34.5 bars H <sub>2</sub>	5	100	[93]
8	LA	Cu-ZrO <sub>2</sub>	methanol	200	34.5 bars H <sub>2</sub>	5	90	[93]
9	LA	Cu-Al <sub>2</sub> O <sub>3</sub>	H <sub>2</sub> O	200	34.5 bars H <sub>2</sub>	5	100	[93]
10	LA	Cu-Al <sub>2</sub> O <sub>3</sub>	methanol	200	34.5 bars H <sub>2</sub>	5	86	[93]
11	LA	Cu-Cr oxide	H <sub>2</sub> O	200	70 bars H <sub>2</sub>	10	90.7	[91]
12	LA	Cu-Fe oxide	H <sub>2</sub> O	200	70 bars H <sub>2</sub>	10	88.9	[92]
13 <sup>a</sup>	ML	Cu-ZrO <sub>2</sub>	methanol	200	34.5 bars H <sub>2</sub>	5	92	[93]
14	ML	Cu-Al <sub>2</sub> O <sub>3</sub>	methanol	200	34.5 bars H <sub>2</sub>	5	88	[93]
15 <sup>b</sup>	EL	10% Ni/Si	--	200	HCOOH	N.D.	40	[87]
16	EL	10% Ni/Si	--	250	HCOOH	N.D.	73	[87]

<sup>a</sup> ML: methyl levulinate.<sup>b</sup> EL: ethyl levulinate.**Table 5**

Production of GVL using other types of catalysts.

No.	Substrate	Catalyst	Solvent	Other conditions	Y <sub>GVL</sub> (%)	Refs.
1	LA	PrO <sub>2</sub>	ethyl ether	250 °C, 44 h, 3 bars H <sub>2</sub>	87	[96]
2	LA	CuCr-oxide	--	190 °C, 1.3 h, 200 bars H <sub>2</sub>	94	[95]
3	LA <sup>a</sup>	Zr-Beta-100	2-propanol	250 °C, 1 bar pressure	>99	[98]
4	LA <sup>a</sup>	Zr-Beta-100	2-pentanol	118 °C, 10 h	96	[98]
5	LA <sup>a</sup>	Zr-Beta-100	cyclohexanol	150 °C, 6 h	82	[98]
6	LA	ZrAl-Beta-100	2-pentanol	118 °C, 6 h	72	[98]
7	LA <sup>b</sup>	ZrO(OH) <sub>n</sub> -400	2-butanol	150 °C, 16 h	41	[98]
8	BL <sup>c</sup>	MgO/Al <sub>2</sub> O <sub>3</sub>	2-butanol	150 °C, 16 h	14.6	[97]
9	BL	CeZrOx	2-butanol	150 °C, 16 h	15.8	[97]
10	BL	ZrO <sub>2</sub>	2-butanol	150 °C, 16 h	84.7	[97]
11	EL	ZrO <sub>2</sub>	Isopropanol	150 °C, 4 h	62.4	[97]
12	LA	Zr-beta	2-butanol	120 °C, 11 h	>98	[99]
13	ML	Zr-beta	2-butanol	120 °C, 5 h	>97	[99]
14	ML	Al-beta	2-butanol	120 °C, 5 h	10.8	[99]
15	Furfural	Zr-beta + Amberlyst-70	2-butanol	120 °C, 24 h	66	[99]
16	Furfural	Zr-beta + H <sub>2</sub> SO <sub>4</sub>	2-butanol	120 °C, 24 h	16	[99]
17	Furfural	Zr-beta + Al-MFI	2-butanol	120 °C, 5 h	78	[99]
18	EL	Zr(OH) <sub>4</sub>	2-butanol	200 °C, 1 h	81.3	[100]
19	EL	Zr(OH) <sub>4</sub>	ethanol	200 °C, 1 h	43.1	[100]
20	ML	Zr(OH) <sub>4</sub>	methanol	200 °C, 1 h	9.4	[100]
21	BL	Zr(OH) <sub>4</sub>	butanol	200 °C, 1 h	28.7	[100]

<sup>a</sup> Zr-Betal-100 (Si/Zr = 100).<sup>b</sup> ZrO(OH)<sub>n</sub>-400: calcination temperature at 400 °C.

catalysts, ZrO<sub>2</sub> catalyst display the highest yield of GVL with 84.7%. Recently, Wang et al. [98] reported that Zr-Beta zeolite was a robust and active catalyst for the Meerwein-Ponndorf-Verley reduction of LA to GVL. In a batch reactor, GVL was formed with the selectivity of >96%. In a continuous flow reactor, >99% yield of GVL was obtained

with a steady space-time-yield of 0.46 mol<sub>GVL</sub> g<sub>Zr</sub><sup>-1</sup> h<sup>-1</sup> within 87 h on the Noble metal catalysts. The high activity of this catalyst was attributed to the presence of Lewis acidic sites with moderate strength. Bui et al. [99] reported an integrated catalytic process for the efficient production of GVL from furfural through sequential

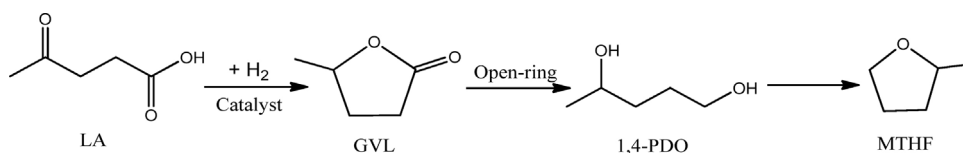
**Table 6**

Production of MTHF from the hydrogenation of LA or GVL.

No.	Substrate	Catalyst	Other reaction conditions	Y <sub>MTHF</sub> (%)	Refs.
1	LA	Ru-complexes	200 °C, NH <sub>4</sub> PF <sub>6</sub> additive, 18 h, 100 bars H <sub>2</sub>	59	[54]
2 <sup>a</sup>	LA	Ru-complexes	160 °C, AIL additive, 18 h, 100 bars H <sub>2</sub>	87	[54]
3	LA	Ru-complexes	160 °C, AIL + NH <sub>4</sub> PF <sub>6</sub> additive, 18 h, 100 bars H <sub>2</sub>	92	[54]
4	LA	80% Cu/SiO <sub>2</sub>	265 °C, 25 bar, 0.513 h <sup>-1</sup> , molar ratio H <sub>2</sub> /LA of 80, 100 h	64	[86]
5	LA	Copper chromite	265 °C, 25 bar, 0.513 h <sup>-1</sup> , molar ratio H <sub>2</sub> /LA of 80, 100 h	36	[86]
6	LA	PdRe/C	200–250 °C, 100 bars of H <sub>2</sub>	90	[107]
7	GVL	30% Cu/Al <sub>2</sub> O <sub>3</sub>	10 mL ethanol, 0.1 g catalyst, 60 bars H <sub>2</sub> , 200 °C, 6 h	7.1	[109]
8	GVL	30 wt% Cu/ZrO <sub>2</sub>	10 mL ethanol, 0.1 g catalyst, 60 bars H <sub>2</sub> , 240 °C, 6 h	91.1	[109]
9	LA	Ru-Starbon	0.3 mL formic acid, 150 °C, microwave irradiation	<15%	[110]
10	LA	Rh-Starbon	0.3 mL formic acid, 150 °C, microwave irradiation	62.1	[110]
11	LA	5% Pd/C	0.3 mL formic acid, 150 °C, microwave irradiation	71.8	[110]
12	LA	5% Pd/C	0.3 mL formic acid, 150 °C, flow rate of 0.1 mL min <sup>-1</sup>	20.4	[110]
13	LA	13% CuO/Al <sub>2</sub> O <sub>3</sub>	0.3 mL formic acid, 150 °C, microwave irradiation	46.2	[110]

<sup>a</sup> Acidic ionic liquid ((4-sulfobutylimidazolium-p-toluenesulfonate).





**Scheme 4.** Hydrogenation of levulinic acid to produce MTHF.

transfer-hydrogenation and hydrolysis reactions catalyzed by zeolites with Brønsted and Lewis acid sites. This is a milestone finding that broads the route for the production of GVL. More recently, a series of low-cost readily-assembled eco-friendly metal hydroxides were examined as catalysts in the synthesis of GVL from biomass-derived ethyl levulinate (EL) via hydrogen transfer reaction [100]. Among these catalysts,  $\text{ZrO}(\text{OH})_2 \cdot x\text{H}_2\text{O}$  was found to be the most active catalyst. EL conversion of 93.6% and GVL selectivity of 94.5% were achieved when 2-propanol was used as a hydrogen donor at 200 °C in 1 h. The typical works of GVL synthesis using other types of catalysts are presented in Table 5. The investigations highlighted herein have successfully identified promising base metal catalysts; however, the number of systems developed is limited. Besides, the optimization of reaction parameters would be important. Arguably, more studies are required to develop a wider range of base metal catalysts, a research effort that could potentially facilitate a more economical GVL production Table 6.

#### 4. Catalytic upgrading of GVL to fuels and chemicals

The attractive properties of GVL have made it suitable and stable for the production of fuels and food additives [101–103]. Jessop et al. [101] reported that GVL has advantages of fewer steps in the processing of biomass compared to other common solvents (e.g., trichloro-methane, THF, and most ionic liquids). Qi et al. [102] reported that GVL can be used as solvent in the dehydration of sugar to produce high value platform molecules (i.e., HMF, LA, and GVL). Mellmer et al. [103] reported the significant increase in reaction rates as well as increased product selectivities using GVL as the solvent in the dehydration of xylose to furfural. In the following section, we will concentrate on fuels and value-added chemicals produced from GVL upgrading.

##### 4.1. Biofuel MTHF

2-methyltetrahydrofuran (MTHF), a highly flammable mobile liquid, is mainly used as a replacement for THF solvent in the specialized applications with its better performances, such as obtaining higher reaction temperature, or easier separation, which is possible due to the solubility of MTHF (13 mg/ml in water). Besides, as with other oxygenated molecules, direct application of GVL as a fuel additive still suffers from several limitations for widespread use in the transportation sector [1,2], such as high water solubility, blending limits for use in conventional combustion engines, possible corrosiveness in storage and lower energy density compared to petroleum-derived fuels. These limitations can be partially alleviated by replacing GVL with MTHF [86,104]. It is reported that MTHF can be blended up to 70% in gasoline [1,34]. Albeit MTHF has a lower heating value than the regular petroleum, it has a higher specific gravity and hence mileage from MTHF blended fuel would be more competitive. Besides, MTHF can significantly reduce the vapour pressure of ethanol when it was co-blended in gasoline [105,106].

The production of MTHF is often performed through the catalytic hydrogenation of LA as shown in Scheme 4. LA is initially hydrogenated to 4-hydroxypentanoic acid that is spontaneously dehydrated to GVL. The produced GVL can be hydrogenated to 1,4-pentanediol (1,4-PDO), which can further be dehydrated to MTHF.

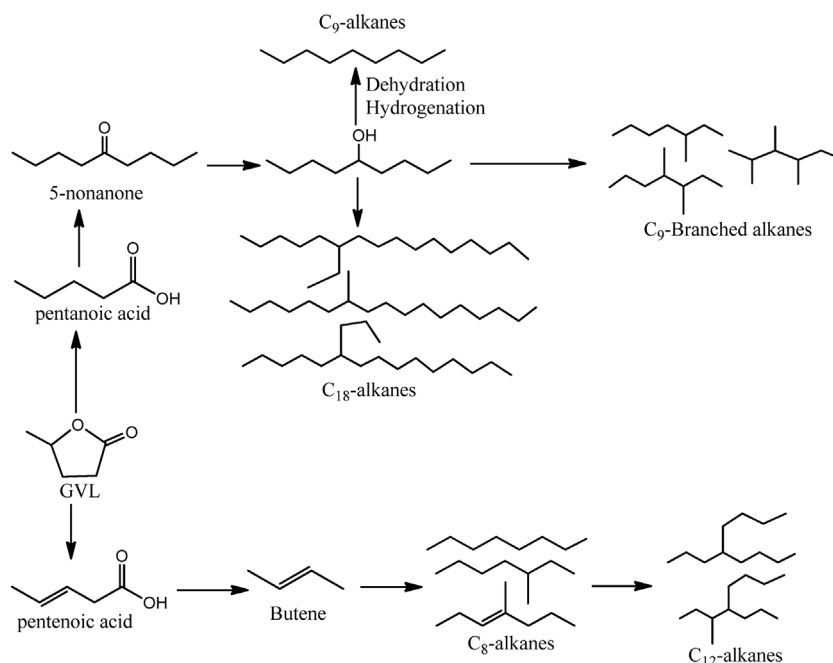
Due to the easy access to the catalytic active center, homogeneous catalyst has displayed very good activity for the production of MTHF. Geilen et al. [54] performed the hydrogenation of LA using Ru-complexes, showing that the selectivity can be tuned to GVL or 1,4-PDO or MTHF depending on the nature of ligands and additives. For example, 1,4-PDO was obtained in a high yield of 95% with triphos as a ligand and MTHF can be produced with 92% yield upon the addition of an acidic ionic liquid. The catalytic production of MTHF using heterogeneous catalyst was pioneered done by Bozell et al. [107] from the hydrogenation of LA using a bifunctional PdRe/C catalyst. Up to 90% yield of MTHF was produced under the conditions of 200–250 °C and 100 bars of H<sub>2</sub>. Recently, direct hydrocyclization of LA to MTHF through GVL intermediate over Cu-derived nanocomposite catalysts in the vapor phase has also been reported by Upare et al. [75,86,108]. They reported the selectivity of MTHF could be tuned by the metal loading applied, where 80 wt% Cu/SiO<sub>2</sub> catalysts could lead to 64% yield of MTHF. Besides, the addition of Ni to the catalyst was found to improve the selectivity of MTHF to 89%.

At present, the biggest challenges for the heterogeneous hydrogenation of LA for the production of MTHF is the high yield of coke produced during the process [37,75,86]. The coke formed has high carbon content and is deficient in H<sub>2</sub>, suggesting that the addition of a hydrogen donor could be useful in limiting the amount of coke. Besides, the variation of reaction parameters and alteration of the catalyst support have a profound influence on catalytic activities. Further research is also required to optimize these important reaction parameters.

##### 4.2. Hydrocarbon fuels

GVL can be upgraded to hydrocarbon fuels by a number of catalytic routes involving hydrogenation, deoxygenation and dehydration reactions combined with C–C coupling reactions as shown in Scheme 5. Upgrading GVL to liquid hydrocarbon fuels often follows two possible routes (Scheme 5). One of them is the production of butenes from pentenoic acid, which can be subsequently oligomerized to higher alkenes [111–113]. Bond et al. [16,111] developed a novel strategy for the efficient production of liquid hydrocarbon fuels from GVL solution without the need for external H<sub>2</sub> using a dual reactor system. In the first reactor system, GVL went through ring opening to produce pentenoic acid isomers with subsequent decarboxylation over a SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst at 36 bars H<sub>2</sub>, wherein the gas mixture of butene isomers and CO<sub>2</sub> was produced. In the second reactor connected in series, the C12 jet fuel would be produced through the oligomerization of butenes when the previously produced gaseous mixture took place over an acidic catalyst (HZSM-5 or Amberlyst70). The final yield of higher liquid alkenes reached 75% when HZSM-5 catalyst (main function of decarboxylation of GVL) and Amberlyst 70 catalyst (used for olefin oligomerization) were combined.

The other route to upgrade GVL (Scheme 5) is via the production of pentanoic acid through ring-opening on acidic sites and further hydrogenation on metal site. The produced pentanoic acid is subsequently ketonized to 5-nonanone, which can be further upgraded to C9-alkanes or C9-branched alkanes or C18-alkanes. The efficient production of pentanoic acid and 5-nonanone in the first two steps are crucial for good yields of final upgraded products. Van den Brink



**Scheme 5.** Routes for the transformation of GVL into liquid alkanes.

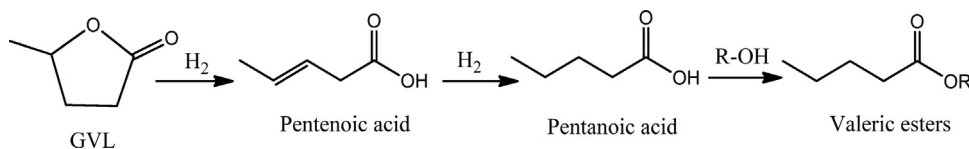
et al. [114] reported the acidic zeolite or silica supported Pt and Ni catalysts efficient for the conversion of GVL into pentanoic acid, where the reaction was performed in the batch reactor system under the conditions of 250 °C, 4 h and 80 bars H<sub>2</sub> in the presence or absence of ethanol. It was very interesting to find 68% yield of pentanoic acid was produced in the absence of ethanol and 71.3% yield of ethyl valerate was formed. Pham et al. [115] have carried out the conversion of GVL to pentanoic acid in a continuous reactor system using a bifunctional acidic niobia catalyst. At 300 °C, 35 bars and a WHSV of 3.1 h<sup>-1</sup>, the initial GVL conversions were higher than 95% with selectivity to pentanoic acid exceeding 80%. Ketonization of two molecules of pentanoic acid yields 5-nonanone along with CO<sub>2</sub> and water. Serrano-Ruiz et al. [106] produced 90% of 5-nonanone with lower ketones (2-hexanone and 3-heptanone) from an aqueous GVL in a single reactor, whereby 0.1% Pd/Nb<sub>2</sub>O<sub>5</sub> (mainly for the production of pentanoic acid) with Ce–Zr (used for the ketonization reaction) were used as catalyst. Once the 5-nonanone was formed, it separated from water spontaneously due to the hydrophobicity. The next step product was the hydrogenation of 5-nonanone into 5-nonanol, which is the precursor for the production of hydrocarbon fuels. The hydrogenation of 5-nonanone to 5-nonanol can be performed under the mild conditions of 50 bar H<sub>2</sub>, 150 °C and Ru/C catalyst. The produced 5-nonanol can be subsequently dehydrated and isomerized over an acid catalyst (e.g., Amberlyst 70) to produce a mixture of C<sub>9</sub> olefins which can be subsequently oligomerized to C<sub>18</sub>–C<sub>27</sub> olefins as a promising diesel fuel. On the other hand, the lower molecular ketones undergo further oligomerization to produce C<sub>6</sub>–C<sub>27</sub> alkenes that can be hydrogenated to the corresponding alkanes as jet fuel or diesel blenders [104]. Although the production of alkanes fuel from GVL has been established, optimization of reaction parameters, increasing the final yields of desired alkanes and reducing the multiple steps still require many additional efforts.

#### 4.3. Valerate esters

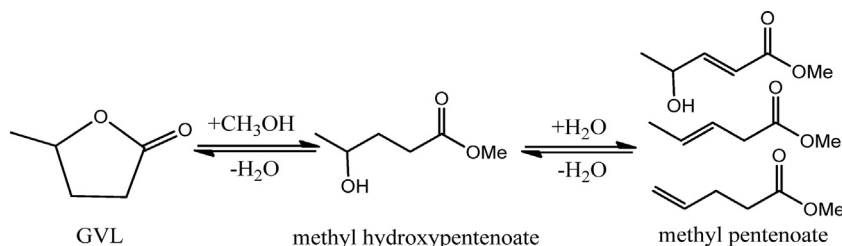
Due to their unique properties, valerate esters have showed promising properties for wide applications as oxygenating fuel components for gasoline and diesel fuels. Valerate esters with

shorter carbon chain (e.g., methyl and ethyl valerate) are suitable for blending with gasoline while the esters with longer chain (e.g., butyl and pentyl) more cater for diesel fuel [116]. Butyl and pentylvalerate have a cetane number close to butanol, they have similar evaporation properties (boiling point and latent heat) close to diesel fuel [116]. Compared with levulinate esters, the valerate esters have a higher energy density due to the higher C/O ratio. These esters are lower in polarity and are thus less miscible with water. They are also more miscible with hydrocarbons of higher chain length, like those present in diesel fuel. Although valerate esters have a lower energy density than FAME, butyl and pentylvalerate show ignition properties and flow characteristics that are compatible with diesel fuel.

The synthesis of valerate esters often involves the hydrogenation of GVL to pentanoic acid and the subsequent esterification of PA with alcohols or glycols to form the corresponding esters as shown in Scheme 6. The formation of pentanoic acid from GVL starts with the ring-opening of GVL to pentenoic acid and subsequent hydrogenation to pentanoic acid (Scheme 6). The process requires a bifunctional acid-metal catalyst. Zeolite supports are often employed for loading of metal nanoparticles due to their adjustable acidity, easy recycle, the potential economic and environmentally benign benefits [117]. Lange et al. [46,118] did some pioneering works and reported that Pt-loaded on SiO<sub>2</sub>-bound H-ZSM-5 catalyst was the most effective catalysts from screening of ~150 catalysts in a continuous high-pressure plug-flow reactor. Over 90% pentanoic acid was produced and this performance can be maintained for more than 1500 h through the simple catalyst regeneration by calcinations in the air. Besides, the authors further demonstrated that GVL could be directly converted into pentylvalerate (20–50% selectivity) using Pt/TiO<sub>2</sub> or Pd/TiO<sub>2</sub> catalysts at 275–300 °C. Serrano-Ruiz et al. [104,106,119] reported a similar strategy to convert GVL to pentanoic acid at yields higher than 92% using a series of Pd/Nb<sub>2</sub>O<sub>5</sub> catalysts. Through the optimization of reaction conditions (Pd loading, temperature, partial hydrogen pressure and WHSV), the metal loading and H<sub>2</sub> pressure were important to inhibit the formation of side products. Comparatively, dispersing the active phases Pt over carbon support (NbCe–C), nearly 90% selectivity to pentanoic acid at 90% conversion of GVL was achieved. Recently, Chan-Thaw et al. [120] reported



Scheme 6. Conversion of GVL to valerate esters.



Scheme 7. Ring opening of GVL into methyl pentenoates.

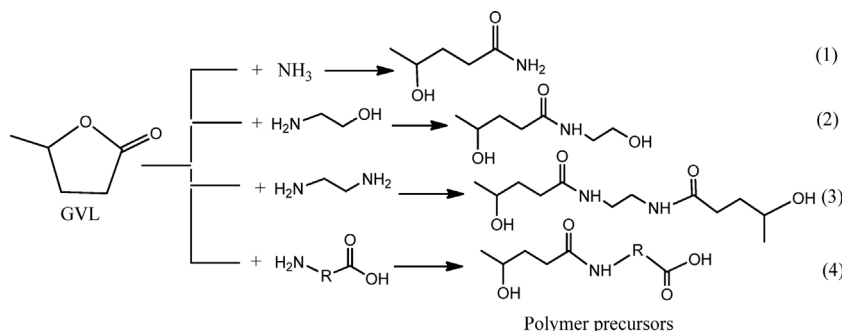
the production of pentylvalerate from GVL and pentanol, and ethyl valerate from GVL and ethanol in a one-pot process using the Cu catalyst loaded on the support of  $\text{SiO}_2\text{-ZrO}_2$ . The reaction took place in alcohol solvent under  $\text{H}_2$  through the nucleophilic addition of the alcohol to the carboxylic group giving hydroxypentanoate, followed by the dehydration and hydrogenation to the saturated ester. Pentylvalerate can be obtained with conversion over 90% and selectivity up to 83% in the pentanol solvent. When ethanol solvent was used, ethyl valerate was formed at the lower selectivity due to the formation of ethyl 4-ethoxy pentanoate and pentenoic esters side products. More recently, Sun et al. [121] reported a bifunctional base-metal catalyst (Co/HZSM-5) was efficient for the conversion of LA into pentanoic acid and ethyl valerate under the batch and fixed-bed reactor system, respectively. Using the same catalyst (Co/HZSM-5), 93% yield of pentanoic acid can be obtained from the hydrogenation of LA at  $80^\circ\text{C}$  in a bed reactor and 97% yield of pentanoic acid and ethyl valerate was produced at  $240^\circ\text{C}$  for 3 h in a batch reactor. While using GVL as substrate in ethanol solvent, ~64.2% ethyl valerate can be produced. So far, the overall yield of valerate esters is still low and many processes are still in the early stage. Ethyl valerates are promising fuels for gasoline, and pentylvalerate could be used in diesel applications. With regard to process integration, one-step conversion of GVL to pentylvalerate with a high activity would be more desirable [122]. To save the cost, the metal content of the catalyst has to be decreased while the selectivity of valerate esters should be maintained.

#### 4.4. Polymers

Some “biopolymers” can be constructed entirely from biomass, whereas others are only partially derived from biomass, a portion of the polymer being derived from petrochemical sources

[40,123,124]. Polymers derived from biomass form a fascinating and increasingly important field of research, for example macromolecules offer differentiated material properties as compared to conventional polymers from fossil feedstock [124–126]. Also, the production of polymers from renewable biomass is more sustainable and feasible than petrochemical source monomers. Biomass-derived GVL can not only be used to produce renewable fuels, but also to make polymers. Lange et al. [21,46,127,128] have performed studies on the ring-opening of GVL to methylpentenoates as shown in Scheme 7. The yield of methylpentenoates can reach 98% at  $200^\circ\text{C}$  and it was easy to be separated since it was more volatile than GVL [128]. The methylpentenoate can be converted to nylon precursors such as caprolactone via hydroformylation, caprolactam via hydrocyanation and adipic acid via hydrocarbonylation [126].

The ring opening of GVL with amine compounds was proposed as a promising strategy to synthesize precursors for the production of new bio-based polymers. Ring-opening of GVL at mild conditions can produce various  $\gamma$ -hydroxy-amides by reacting with mono- or di-functional aliphatic primary- or secondary amines as shown in Scheme 8. The lactone ring opens via a nucleophilic addition of the “hard” amine to the lactone carbonyl and results in the cleavage of the cyclic ester with the formation of an amide [125,126]. The synthesis process is simple through mixing amine compound (ammonia, 2-aminoethanol, 1,2-diaminoethane, or piperazine) with an excess amount of GVL under solvent-free conditions for several hours [125]. The final product was extracted by using the mixture of hexane and diethyl ether (1:1 v/v). A combined analysis of  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR analysis, FTIR and Elemental Analysis confirmed the structure and composition. Two important GVL-derived diols (Scheme 8), i.e., *N,N'*-1,2-ethanediyldis-(4-hydroxy-pentanamide) (3) and 4-hydroxy-*N*-(2-hydroxyethyl)-



Scheme 8. Synthetic routes for bio-based polymers derived from LA.

pentanamide(4) obtained by the ring-opening of GVL with ethylenediamine and aminoethanol, respectively, can be applied as green polymer precursors. Besides, a set of new polyurethanes (polymer precursor) can be produced through the condensation between GVL and different monomers. The variation in the chemical structure of polyurethane precursors enables the manufacture of materials with a wide range of thermal and mechanical properties. Ring-opening of GVL is a promising novel pathway to prepare bifunctional monomers suitable for polymer synthesis [125]. There are many possibilities in the production of the promising polymer with special functional groups using GVL by varying the structure of the amines. However, many of these processes are still in early stages and the overall yields are still low. Lab-scale experiments are needed to identify crucial parameters which have determining effects on the yield towards the desirable product.

## 5. Conclusions and future perspectives

In general, we conducted a comprehensive review of current technologies and mechanisms of GVL production as well as the catalytic upgrading of GVL to fuels and value-added chemicals. Over the past several years there has been a rapid acceleration of studies aimed at understanding how to tailor homogeneous, heterogeneous catalysts and the reaction systems utilizing them for the efficient conversion of biorenewable feedstocks to GVL as well as the upgrading of GVL to fuels and value-added chemicals.

(i) Current production of GVL is mainly from the hydrogenation of LA intermediate. A cost-effective process for producing LA from lignocellulosic biomass in a large scale is still required. Replacement of mineral acid in the production of LA by recyclable heterogeneous catalysts would be more compatible with a sustainable environment. Purification and separation of LA in high yields would be more ideal for the production of GVL. Besides, the development of alternative catalysts instead of Noble metal catalysts for the production of GVL with minimum utilization of external hydrogen resources would be more economically viable.

(ii) In the production of MTHF and alkanes, the zeolite support has been widely used due to their adjustable acidic properties, high surface area and relatively high hydrothermal stability. However, the supported metal nanoparticles are often located on the surface due to the microporous sizes. Enlarging micropores into mesopore would increase the surface area and locate the active sites inside the mesoporous channels, which can efficiently prevent the potential metal leach and be elegantly fruitified in shape-selective effect, possibly increasing the selectivity.

(iii) To achieve the necessary heterogeneous catalyst advancements, more fundamental understanding about how catalysts can be designed specifically for converting biorenewable feedstocks to GVL is still needed. The targeted catalysts should be equipped with a variety of catalytic functions, including acidic sites, basic sites, and metal hydrogenation sites, to achieve the goal. By identifying, optimizing and tuning important catalyst parameters, more effective catalytic materials can be designed with the improved selectivity to desirable products and reducing the coke formation.

(iv) Bio-polymers can provide an alternative to a number of petroleum-derived polymers. The productions of polymers from biomass are still in early developments and the overall yield is still requiring improvement. Future studies should pay more attention to product design through rationally varying the structure of the amines and identifying important catalytic parameters which have determining effects on the yield of polymers.

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